

Self-Consistent Field Calculations Using Two-Body Density Functionals for Correlation Energy Component: I. Atomic Systems

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ABSTRACT: Self-consistent field calculations are done using two-body density functionals for the correlation energy. The corresponding functional derivatives are obtained and used in pseudo-eigenvalue equations analogous to the Kohn–Sham ones. The examples studied include atomic systems from He to Ar. The values obtained for ionization potentials, electron affinities, dipole polarizabilities, and virial ratios from these calculations are given, and the effect of exchange is addressed. The results obtained are in good agreement with experimental values, and are of the same quality as those given by accurate exchange-correlation functionals. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1887–1898, 1998

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Introduction

In a recent article¹ we derived expressions for the correlation energy of atoms and molecules, written as functionals of the two-body density

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matrix in $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{R}$, $\rho_2^0(\mathbf{R})$, and the charge density, $\rho^0(\mathbf{R})$, corresponding to a suitable reference wave function. These functionals (which, in what follows, will be called two-body density functionals, or TBDF), were obtained within the correlation factor approach by expressing the spin-free second-order reduced density matrix as:

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \rho_2^0(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \cdot [1 + F(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)] \quad (1)$$

Here, ρ_2^0 is the second-order reduced density matrix of a reference wave function (which can be just one Slater determinant, or a combination of several determinants), whereas F is the correlation factor that introduces the corrections needed to obtain the exact ρ_2 from ρ_2^0 . Therefore, the exact energy may be cast in the form:

$$E = E^0 + E_c \quad (2)$$

where E^0 is the energy associated to ρ_2^0 , and E_c is the remaining energy that represents the residual correlation energy or, simply, correlation energy. Imposing the constraint that the virial theorem must be satisfied by both E and E^0 , the correlation energy in eq. (2) takes the form:¹

$$E_c = 2\pi \iint \rho_2^0(\mathbf{R}, r) F(\mathbf{R}, r) r dr d\mathbf{R} + \Delta \quad (3)$$

where:

$$\rho_2^0(\mathbf{R}, r) = \frac{1}{4\pi} \int \rho_2^0(\mathbf{R}, \mathbf{r}) d\Omega_r \quad (4)$$

is the \mathbf{r} -angular-averaged two-body density, with $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ being the center of mass and relative coordinates, respectively. The first component in eq. (3) represents the electron repulsion correlation energy, whereas Δ is the nuclear attraction contribution:

$$\Delta = \frac{1}{2} \int v(\mathbf{R}) [\rho(\mathbf{R}) - \rho^0(\mathbf{R})] d\mathbf{R} \quad (5)$$

where $v(\mathbf{R})$ is the external potential in which the electrons move, and $\rho(\mathbf{R})$ is the exact charge density of the system. The difference between ρ and ρ^0 is small, even when the last one is the charge density belonging to a Hartree–Fock (HF) wave function.² For this reason, eq. (5) generally represents a small contribution to the correlation energy given by eq. (3) that to a good approximation level can be neglected.¹ The expression of $\rho_2^0(\mathbf{R}, r)$ was approximated by a *corrected Gaussian summation*:

$$\rho_2^0(\mathbf{R}, r) = \rho_2^0(\mathbf{R}, 0) \cdot P(\mathbf{R}, r) \cdot \exp(-r^2/\gamma(\mathbf{R})) \quad (6)$$

where $\rho_2^0(\mathbf{R}, 0) \equiv \rho_2^0(\mathbf{R})$ is the two-body density of the reference wave function evaluated at $r = 0$. $P(\mathbf{R}, r)$ is a polynomial in powers of r correcting the Gaussian summation approximation to the Taylor expansion of $\rho_2^0(\mathbf{R}, r)$. Finally, $\gamma(\mathbf{R})$ is a function obtained from the hierarchy condition

between ρ_2^0 and ρ^0 , namely:

$$\rho^0(\mathbf{R}) = \frac{8\pi}{N-1} \int_0^\infty r^2 \rho_2^0(\mathbf{R}, r) dr \quad (7)$$

The correlation factor F was modeled using two extensions¹ to that of Colle and Salvetti.^{3,4} The corresponding two sets of functionals that arise from each of these two correlation factors are labeled “F1” and “F2” in what follows (see Appendix and ref. 1 for details regarding the explicit expressions of the correlation factors). The polynomial $P(\mathbf{R}, r)$ entered in eq. (6) was developed to several orders of r , giving rise to different *levels of development* for each set of functionals F1 and F2.

The functionals obtained in ref. 1 cover any kind of reference wave function, including those built from many Slater determinants. This fact is, in our opinion, the more important characteristic of those functionals. However, in this study, they are applied using a one-determinant reference wave function. Under this condition, our correlation functionals behave as authentic density functionals, and they can be handled in self-consistent equations of the Hartree–Fock–Kohn–Sham (HFKS) type.⁵ Therefore, in this series of articles, the TBDFs are dependent only on the spin components of the reference charge density, due to the fact that, for a one-determinant wave function:

$$\rho_2^{det}(\mathbf{R}, 0) = \rho_\alpha^{det}(\mathbf{R}) \rho_\beta^{det}(\mathbf{R}) \quad (8)$$

where the superscript “*det*” refers to the Slater determinant used to build ρ_2 , ρ_α , and ρ_β . The parameters needed in the final expressions of the functionals were fitted to reproduce the atomic correlation energies from He to Ne.¹

From these data, the set of local correlation energy functionals derived in ref. 1 can be used to approximate the total energy of any atom or molecule by:

$$E[\rho_\alpha^{det}, \rho_\beta^{det}] = E_{det}[\rho_\alpha^{det}, \rho_\beta^{det}] + E_c[\rho_\alpha^{det}, \rho_\beta^{det}] \quad (9)$$

with E_{det} being the energy provided by a Slater determinant, whereas E_c stands for one of the TBDFs. The orbitals that expand ρ_α^{det} and ρ_β^{det} can be obtained by applying the variational principle to eq. (9), subject to suitable orthonormalization conditions. The corresponding HFKS pseudo-eigenvalue equations must be solved iteratively by using a self-consistent field (SCF) procedure. This has been done here by applying the restricted-open-shell Hartree–Fock scheme of McWeeny and

Diercksen,⁶ including the correlation contribution arising from the functional derivatives of the TBDF with respect to ρ_{α}^{det} and ρ_{β}^{det} . The explicit expressions for these functional derivatives (also known as correlation potentials) are given in the Appendix.

Besides the TBDF just mentioned, we have also used other correlation energy functionals in eq. (9). We have chosen the local correlation energy functional obtained by Vosko, Wilk, and Nusair (VWN)⁷ and the nonlocal one derived by Lee, Yang, and Parr (LYP),⁸ which is a simplification of that deduced by Colle and Salvetti.³ In principle, the exchange contribution in E_{det} can be substituted by one of the several exchange density functionals present in the literature. This is the standard procedure followed when applying the Kohn–Sham formalism. For this reason, we have also tested the effect of using the Becke exchange functional⁹ when solving the corresponding SCF problem. To check the influence of the basis set on the results, we carried out calculations using the 6-311G** and ANO-TZ^{10,11} basis sets. The properties reported are the ionization potential (I), electron affinity (A), static isotropic dipole polarizability ($\bar{\alpha}$), and virial ratios for the set of atoms ranging from He to Ar. These calculations were performed using the Gaussian-92 code.¹² The results of the calculations are given in the second section, and analyzed in the third section. The main conclusions are summarized in the final section.

Calculations

Here, we give the results of the SCF calculations just mentioned. We have selected the TBDFs that correspond to the highest development levels considered in ref. 1. Therefore, among those functionals corresponding to the F1 set we have chosen the highest level, F1(6), which has five independent parameters and level five, F1(5), with only four parameters. In regard to the F2 set, we have chosen the highest level of development, F2(5), with four parameters entering in the functional. The explicit form of these functionals can be found in ref. 1 (see also Appendix).

The ionization potential is given by $I = E[N - 1] - E[N]$, and the electron affinity by $A = E[N] - E[N + 1]$, where $E[K]$ is the nonrelativistic ground-state total energy of the K -electron system. The exact I are taken from refs. 13 and 14, where the relativistic contribution corrections are subtracted. The experimental A values from ref. 15

are also corrected by the relativistic contributions from ref. 16. Both I and A are affected slightly by the relativistic effects, with changes always less than or equal to 0.01 eV. Both sets of exact values are listed in Table I, together with HF values using different basis sets. Although the Hartree–Fock I values are in good correspondence with the exact ones, the rather poor total energies for the negative ions, obtained with the HF wave function, explain the poor results for A . As it is well known, the wrong description of the loosely bound electron in the negative ion is responsible for this situation. Accurate A values are difficult to achieve, even for very complete wave functions. Here we will assess the improvement of I and A , when correlation is included by the functionals mentioned in the Introduction. Tables II and III list the values of I and A , respectively, using the F1, F2, VWN, and LYP correlation functionals and HF exchange.

The static dipole polarizability of the neutral atoms has also been calculated. This quantity describes the response, in lowest order, of the field of strength of the electron cloud to an external dc electric field. The electric dipole moment, $\mathbf{p} = -\sum_{i=1}^N \mathbf{r}_i$ (the summation is on the position coordinates \mathbf{r}_i of the N electrons in the system), of an atom or molecule in the presence of a uniform electric field \mathbf{F} can be expanded as:

$$\mathbf{p} = \mathbf{p}_0 + \boldsymbol{\alpha} \cdot \mathbf{F} + \frac{1}{2}\boldsymbol{\beta}:\mathbf{F}^2 + \frac{1}{6}\boldsymbol{\gamma}:\mathbf{F}^3 + \dots \quad (10)$$

For atoms and homonuclear molecules there is no permanent dipole moment \mathbf{p}_0 and, for spherically symmetric states, $\boldsymbol{\beta}$ is zero. Thus, one is generally concerned with the polarizability, $\boldsymbol{\alpha}$, a second-rank tensor represented by a 3×3 matrix. If the electric field direction is chosen to be along the axes of symmetry of the atom, the off-diagonal components vanish, and $\alpha_{xx} = \alpha_{yy}$. The two independent polarizability quantities that remain are frequently expressed in terms of an isotropic (the average polarizability) $\bar{\alpha} = \frac{1}{3}(2\alpha_{xx} + \alpha_{yy})$, and an anisotropic part $\alpha_{zz} - \alpha_{xx}$. Here, we concentrate on $\bar{\alpha}$.

The components of the polarizability can be obtained from the derivative of the induced dipole moment with respect to the electric field \mathbf{F} . The derivative is calculated numerically from the solutions of the SCF equations, including the static electric potential $\mathbf{F} \cdot \mathbf{r}$. The value used for the electric field, $9.8 \times 10^8 \text{ V m}^{-1}$, is small enough so that all linear effects are dominant, and large enough to avoid the numerical noise. The “exact” values of $\bar{\alpha}$ listed in Table I, are the recommended values of

TABLE I. Hartree–Fock Ionization Potentials (eV), Electron Affinities (eV), and Static Dipole Polarizabilities (Å³) Using Different Basis Sets (Exact Values of These Properties Are Also Given).

Z	I				A				$\bar{\alpha}$			
	B1 ^a	B2 ^b	B3 ^c	Ex. ^d	B1	B2	B3	Ex. ^e	B1	B2	B3	Ex. ^f
2	23.45	23.46		24.59	< 0	< 0	< 0	< 0	0.09	0.19	0.22	0.21
3	5.34	5.34	5.34	5.39	< 0	< 0	< 0	0.62	25.01	25.08	15.96	24.30
4	8.05	8.05	8.05	9.32	< 0	< 0	< 0	< 0	6.57	6.77	7.77	5.60
5	7.94	7.93	7.93	8.30	< 0	< 0	< 0	0.28	2.45	3.26	3.43	3.03
6	10.80	10.79	10.79	11.26	0.04	0.55	0.55	1.27	1.20	1.78	1.74	1.76
7	13.99	13.97	13.96	14.53	< 0	< 0	< 0	< 0	0.68	1.08	1.00	1.10
8	11.98	11.98	11.89	13.62	< 0	< 0	< 0	1.47	0.30	0.70	0.73	0.80
9	15.75	15.71	15.72	17.42	0.26	1.31	1.36	3.41	0.15	0.48	0.53	0.56
10	19.85	19.87	19.85	21.56	< 0	< 0	< 0	< 0	0.08	0.32	0.39	0.40
11	4.94	4.95	4.95	5.14	< 0	< 0	< 0	0.55	27.89	28.12	18.67	23.60
12	6.61	6.61	6.60	7.65	< 0	< 0	< 0	< 0	11.97	12.06	14.13	10.60
13	5.50	5.50	5.50	5.99	< 0	0.04	0.02	0.45	5.27	9.27	10.97	8.34
14	7.98	7.65	7.65	8.15	0.79	0.96	0.95	1.40	2.91	5.71	6.81	5.38
15	10.22	10.04	10.04	10.49	< 0	< 0	< 0	0.76	1.91	3.76	4.42	3.63
16	9.06	9.09	9.03	10.36	0.93	0.90	0.90	2.09	1.13	2.83	3.44	2.90
17	11.84	11.79	11.82	12.97	2.58	2.53	2.57	3.64	0.71	2.10	2.61	2.18
18	14.78	14.74	14.78	15.76	< 0	< 0	< 0	< 0	0.51	1.59	1.98	1.64

^a6-311G** basis set.
^bANO-TZ basis set.
^cNumerical HF calculation of ref. 24.
^dExperimental data corrected by relativistic effects, from refs. 13 and 14.
^eExperimental data from ref. 15, corrected by relativistic effects taken from ref. 16.
^fRecommended values from ref. 17.

ref. 17. For recent advances in experimental and theoretical calculation of polarizabilities see refs. 18–21 and references therein.

As Table I shows, *ab initio* results of this property are strongly dependent on the basis set employed.^{22,23} Accurate results are obtained only with the use of large, extended basis sets, involving polarization functions. Not only the 6-311G**, but even the accurate numerical near-limit HF wave function of Fraga et al.²⁴ fail to give good results for second-row atoms. The best results, at the HF level, are obtained with the ANO-TZ basis set of refs. 10 and 11. This can be extended to the correlated SCF calculations and to the values of the rest of the properties. Hence, only the results of calculations employing this basis set are reported in Tables II–VI. Table IV shows the isotropic static dipole polarizabilities of He to Ar, obtained with the correlation functionals mentioned in the Introduction, and using the HF exchange. To analyze the effect of using the Becke exchange we performed calculations with this exchange formula and the aforementioned functionals. The values obtained for *I*, *A*, and $\bar{\alpha}$ are listed in Table VI.

Finally, the virial ratios obtained from:

$$-\frac{V}{T} = 1 + \frac{-E_{SCF}}{T_{SCF} - E_c}$$

(11)

are listed in Table V. This equation results by approximating the exact kinetic energy *T* by *T*_{SCF} − *E*_{*c*}, where *E*_{SCF} is the total SCF energy, whereas *T*_{SCF} and *E*_{*c*} are the kinetic SCF (one-determinant), and the correlation contribution to it, respectively. This equation is justified when using our correlation energy functionals (F1 or F2), because the virial theorem has been used in their deduction and they provide a good approximation to the exact (Löwdin’s definition of) correlation energies. The virial ratios have also been calculated for the rest of the functionals by using eq. (11) and both the Hartree–Fock and Becke exchange. The results are given in Table V. All are good estimates of the virial ratio, in accordance with the fact that correlation slightly modifies the electron density. However, the virial ratios obtained using Becke’s formula are not as good as those using the Hartree–Fock-type exchange, because Becke’s results devi-

TABLE II.
HFKS Ionization Potentials (eV) Using Several Correlation Energy Functionals and the ANO-TZ Basis Set.^a

Z	This work					Other work			
	F1(6)	F2(5)	F1(5)	VWN	LYP	LSD ^b	PW ^c	OEP ^d	LSD-GX-SIC ^e
2	24.60	24.60	24.60	25.73	24.65	24.27	24.56	25.03	25.02
3	5.55	5.43	5.66	5.79	5.50	5.45	5.55	5.46	5.35
4	9.13	9.37	8.96	9.45	8.96	9.01	9.14	9.11	8.99
5	8.57	8.71	8.50	8.96	8.47	8.57	8.53	8.87	8.14
6	11.44	11.62	11.31	11.83	11.32	11.67	11.56	12.10	11.25
7	14.59	14.77	14.43	15.02	14.46	14.92	14.82	15.36	14.50
8	13.68	13.74	13.68	13.96	13.36	13.82	13.90	14.04	13.21
9	17.33	17.42	17.27	17.60	17.01	17.94	17.87	18.31	17.29
10	21.40	21.52	21.28	21.68	21.11	22.10	21.99	22.43	21.48
11	5.40	5.54	5.22	5.43	5.21	5.31	5.26	5.31	5.293
12	8.01	8.63	7.53	7.85	7.48	7.70	7.81	7.73	7.70
13	6.27	6.54	5.99	6.34	5.89	5.98	5.95	6.04	5.61
14	8.36	8.57	8.11	8.52	8.05	8.21	8.19	8.35	7.82
15	10.69	10.83	10.46	10.93	10.42	10.51	10.51	10.66	11.02
16	11.00	11.35	10.62	10.75	10.25	10.49	10.44	10.72	10.18
17	13.53	13.81	13.20	13.38	12.88	13.18	13.11	13.46	12.82
18	16.34	16.57	16.05	16.29	15.79	15.92	15.86	16.18	15.55
mre ^f	2.7	4.2	1.5	4.0	1.4	1.8	1.6	3.4	2.1

^a The last entry gives the mean relative error for the whole set of atoms with respect to the exact values listed in Table I. Values from other sources are also included.
^b From ref. 25.
^c Results from the PW-GGA-IIA functional of ref. 25.
^d Results with the OEP-LSDXCSCA method of ref. 26.
^e Results with the LSD-GX-SIC-GWB scheme, using the VWN correlation functional, from ref. 30.
^f $mre = 100 / n \times \sum_{i=1}^n |I_i^{theor} - I_i^{ex}| / I_i^{ex}$.

TABLE III.
HFKS Electron Affinities (eV) from Several Correlation Energy Functionals Using ANO-TZ Basis Set.

Z	This work					Other work ^a			
	F1(6)	F2(5)	F1(5)	VWN	LYP	LSD	PW	OEP	LSD-GX-SIC
3	0.59	1.15	0.42	0.77	0.43	0.58	0.59	0.56	0.54
5	0.19	0.40	0.05	0.41	0.01	0.66	0.55	0.66	0.22
6	1.04	1.25	0.88	1.32	0.86	1.67	1.55	1.69	1.19
8	0.91	1.10	0.76	1.00	0.56	1.93	1.82	1.77	1.11
9	2.69	2.90	2.52	2.82	2.37	3.97	3.81	3.74	3.13
11	0.90	1.69	0.48	0.73	0.42	0.58	0.66	0.58	0.56
13	0.55	0.77	0.32	0.61	0.22	0.60	0.56	0.63	0.31
14	1.47	1.63	1.26	1.62	1.18	1.51	1.49	1.59	1.21
15	1.20	1.69	0.77	0.91	0.51	0.91	0.85	—	—
16	2.45	2.84	2.07	2.25	1.83	2.34	2.25	2.49	2.02
17	3.97	4.29	3.63	3.86	3.43	3.85	3.76	3.99	3.53
mre ^b	26.2	58.7	24.8	22.1	35.6	28.1	21.4	30.2	12.5

^a See footnotes to Table II.
^b $mre = 100 / n \times \sum_{i=1}^n |A_i^{theor} - A_i^{ex}| / A_i^{ex}$.

TABLE IV.
HFKS Isotropic Static Dipole Polarizabilities (Å³)
from Several Correlation Energy Functionals Using
the ANO-TZ Basis (Values from Accurate *Ab Initio*
Calculations Also Included).

Z	This work					Other work ^a
	F1(6)	F2(5)	F1(5)	VWN	LYP	
2	0.19	0.19	0.19	0.19	0.19	
3	24.55	24.57	24.61	24.34	23.04	
4	6.57	6.71	6.57	6.43	6.50	
5	3.10	3.14	3.07	3.00	3.06	
6	1.68	1.69	1.67	1.63	1.66	1.69
7	1.02	1.03	1.02	1.00	1.01	1.08
8	0.68	0.68	0.67	0.66	0.67	0.80
9	0.47	0.47	0.46	0.46	0.46	0.55
10	0.32	0.32	0.32	0.32	0.32	0.40
11	26.09	25.67	26.53	25.72	24.20	
12	11.43	11.49	11.48	11.29	11.24	
13	8.53	8.53	8.65	8.28	8.57	
14	5.41	5.42	5.44	5.27	5.41	5.41
15	3.61	3.62	3.62	3.53	3.61	3.65
16	2.71	2.76	2.70	2.67	2.73	2.90
17	2.03	2.06	2.02	2.00	2.04	2.17
18	1.55	1.58	1.54	1.53	1.55	1.64
mre ^b	7.6	7.3	8.2	8.4	7.4	1.0

^aCCSD(T) results for Ne and Ar taken from ref. 18. The rest
are CASPT2 values from ref. 20.
^bmre = 100/*n* × Σ_{*i*=1}^{*n*} |α_{*i*}^{theor} − α_{*i*}^{ex}|/α_{*i*}^{ex}.

ate from those obtained with the last one, for which the virial theorem is fulfilled exactly. The best results for the whole set of functionals are those given by F1 and F2 functionals, which were deduced assuming the virial theorem.

Discussion

IONIZATION POTENTIALS

Tables I and II show that the inclusion of correlation improves the results obtained with respect to the Hartree–Fock data regardless of which correlation functional is employed. Both F1(5) and LYP give extremely good results, with a mean relative error (mre = 100/*n* Σ_{*i*=1}^{*n*} |*I*_{*i*}^{theor} − *I*_{*i*}^{ex}|/*I*_{*i*}^{ex}; *n* being the number of atoms under consideration) of only 1.5% and 1.4%, respectively. F1(6), VWN, and F2(5) give also good estimates for both first- and second-row atoms, with mre values of 2.7%, 4.0%, and 4.2%, respectively. The remarkably good results of F1(6) and F2(5) for first-row atoms can be seen as a consequence of their parameterization, which has been performed using this set of atoms.¹ As a side effect, F1(6) and F2(5) seem to be overparameterized, thus giving rather poor *I* results for second-row atoms.

TABLE V.
Virial Ratios from Eq. (11) Using HF and Becke Exchange Functionals.

Z	HF					Becke		
	F1(6)	F2(5)	F1(5)	VWN	LYP	F1(5)	VWN	LYP
2	1.9978	2.0004	1.9953	2.0240	2.0120	1.9948	2.0234	2.0114
3	1.9993	2.0000	1.9986	2.0124	2.0055	2.0038	2.0177	2.0108
4	1.9983	1.9996	1.9978	2.0104	2.0042	2.0057	2.0184	2.0122
5	1.9989	1.9996	1.9983	2.0081	2.0032	2.0037	2.0135	2.0087
6	1.9992	1.9996	1.9987	2.0066	2.0026	2.0026	2.0104	2.0066
7	1.9995	1.9998	1.9992	2.0055	2.0023	2.0023	2.0086	2.0054
8	1.9995	1.9997	1.9992	2.0049	2.0023	2.0019	2.0076	2.0050
9	1.9995	1.9997	1.9994	2.0043	2.0022	2.0017	2.0067	2.0046
10	1.9997	1.9999	1.9997	2.0040	2.0022	2.0017	2.0061	2.0043
11	1.9998	2.0000	1.9997	2.0041	2.0022	2.0035	2.0078	2.0060
12	1.9997	1.9998	1.9996	2.0034	2.0018	2.0028	2.0066	2.0051
13	1.9997	1.9998	1.9997	2.0030	2.0016	2.0024	2.0058	2.0043
14	1.9997	1.9998	1.9998	2.0027	2.0014	2.0022	2.0051	2.0039
15	1.9998	1.9999	1.9998	2.0024	2.0013	2.0019	2.0045	2.0034
16	1.9998	1.9999	1.9998	2.0023	2.0012	2.0017	2.0041	2.0031
17	1.9998	1.9999	1.9998	2.0021	2.0011	2.0015	2.0038	2.0028
18	1.9998	1.9999	1.9998	2.0019	2.0011	2.0011	2.0032	2.0024

TABLE VI.

Ionization Potentials (eV), Electron Affinities (eV), and Isotropic Dipole Polarizabilities (\AA^3) for Several Correlation Energy Functionals Using Becke Exchange and ANO-TZ Basis.

Z	I			A			$\bar{\alpha}$		
	F1(5)	VWN	LYP	F1(5)	VWN	LYP	F1(5)	VWN	LYP
2	24.64	25.76	24.69				0.23	0.22	0.23
3	5.68	5.81	5.53	0.43	0.78	0.44	22.12	21.48	20.80
4	8.98	9.46	8.98				6.42	6.25	6.37
5	8.65	9.10	8.63	0.51	0.80	0.44	3.51	3.36	3.48
6	11.39	11.91	11.41	1.36	1.76	1.33	2.00	1.92	1.98
7	14.49	15.07	14.52				1.24	1.19	1.23
8	14.46	14.73	14.16	1.97	2.20	1.79	0.85	0.83	0.85
9	17.95	18.27	17.71	3.75	4.04	3.62	0.59	0.58	0.59
10	21.84	22.23	21.66				0.37	0.37	0.37
11	5.37	5.59	5.36	0.53	0.78	0.48	22.57	21.50	20.79
12	7.68	7.99	7.63				10.70	10.49	10.51
13	5.96	6.32	5.87	0.45	0.70	0.34	10.01	9.34	9.83
14	8.02	8.42	7.95	1.29	1.61	1.20	6.25	5.96	6.18
15	10.25	10.70	10.20	1.12	1.26	0.88	4.17	4.02	4.14
16	10.78	10.92	10.43	2.32	2.50	2.10	3.10	3.05	3.13
17	13.22	13.41	12.91	3.72	3.95	3.54	2.29	2.27	2.32
18	15.84	16.07	15.58				1.70	1.69	1.71
mre	2.4	5.0	1.9	21.5	48.0	17.3	9.6	7.5	10.2

In Table II we include the best results obtained from recent Kohn–Sham calculations by combining different exchange–correlation schemes. These include the local (LSD) and “semilocal” (PW GGA-IIA) functionals reported in ref. 25, those from ref. 26 (OEP-LSDXCSICA) using the optimized effective potential (OEP) method^{27,28} applied to the Perdew–Zunger LSD-SIC functional,²⁹ and those from ref. 30 (LSD-GX-SIC-GWB) using the generalized-exchange local-spin-density functional scheme^{31,32} applied to the VWN functional.⁷ The mean relative errors (mre) from these calculations are 1.8% for LSD, 1.6% for PW GGA-IIA, 3.3% for OEP-LSDXCSICA, and 2.1% for LSD-GX-SIC. All of these are also very accurate, with an average quality similar to that achieved by the calculations just discussed.

ELECTRON AFFINITIES

The whole set of functionals is able to predict correctly the electron affinity for those systems, such as Li, B, O, Na, and P, for which HF predicts no ionization. The increase of A is usually explained by noting that correlation acts mainly between electrons with antiparallel spins, and the number of antiparallel pairs increases in the anion.³³ When compared with the exact values,

the results obtained for A are not as impressive as those for the ionization potential. However, the improvement over the Hartree–Fock A is greater than that achieved for I . In particular, F1(5) and VWN give good values for A ; although they do not reach the extremely good results of accurate *ab initio* calculations,^{34,35} the computational effort is much less. All the results in Table III were obtained by using a one-determinant wave function, and hence they cannot take account for the multi-determinant character needed to describe the non-dynamical correlation due to the loosely bound added electron, which is especially important for Li^- , Na^- , B^- , O^- , and Al^- anions.³⁶ This explains the rather poor A obtained for the corresponding neutral atoms. These data are also supported by the results obtained from the HFKS calculations listed in Table III. From a comparison of the mre values shown in Table III, we deduce that the best results are those given by the F1(5) and VWN functionals, together with those provided by the LSD-GX-SIC scheme.

DIPOLE POLARIZABILITIES

The overall accuracy of the calculations for the dipole polarizabilities is very good, with minor dependencies on the functional used and with mre

(He to Ar) values ranging from 7.3% for F2(6) to 8.4% for VWN.

The results from the whole set of functionals reflect the lack of nondynamical effects pointed out by Werner and Meyer,²² and Reinsch and Meyer.^{37,38} Using the finite perturbation method of Cohen and Roothaan³⁹ to determine atomic and molecular polarizabilities, together with two types of wave functions, PNO-CI and PNO-CEPA, these investigators noted two competing electron correlation effects in their calculations:

1. Unoccupied low-lying *p*-orbitals make possible a very effective angular correlation. If one wants to describe a state in which the two *s*-electrons tend to keep apart from each other by preferring a geometrical configuration on different sides of the nucleus, one has to admix configurations to the ground state with the two *s*-electrons excited into two *p*-orbitals. When there are low-lying unoccupied *p*-orbitals in the atom, this type of correlation is favored, in contrast to the case where the excitation is energetically more expensive. This preference of opposite configurations will lead to a reduction of the shielding of the nuclear potential, and thus a contraction of the valence shell and a reduction of the polarizability. This effect dominates in the left-hand side of rows of the periodic table, because they have empty *p*-orbitals available, and is responsible for the poor results obtained by the one-determinant SCF calculations for Be and Na.
2. Electrons tend to avoid each other by one keeping nearer to the nucleus and the other farther away (in/out correlation). This is achieved by configurations using orbitals with additional radial nodes and is more effective for a more diffuse distribution, because, in this case, the excitation energies are lower. This effect dominates in the right-hand side of rows of the periodic table, and also explains the lack of accuracy of the results shown in this work for atoms O to Ne and S to Ar.

Accurate results from ref. 20 for the C—F and Si—Cl sets, using the second-order perturbation method for single-state multireference wave functions generated in complete-active-space self-consistent field (CASPT2) are included in Table IV,

together with those using *ab initio* pseudopotentials at the CCSD(T) level¹⁸ for Ne and Ar. While the results using correlation functionals are of the same quality as those indicated earlier for C, N, Si, and P, effect 2 (above) is responsible for the loss of agreement between them on O, F, Ne, S, Cl, and Ar.

EFFECT OF EXCHANGE

We have tested the influence of the exchange in the calculations of the previous properties by using the Becke exchange functional⁹ instead of the Hartree–Fock one. The results are given in Table VI.

The effect of exchange on *I* has been studied previously by Cordero et al.⁴⁰ Their results show that the Becke exchange gives *I* values greater than Hartree–Fock ones, for Li to Ar, with the exceptions of B, Al, P, and Ar. This trend can be seen in Table VI (except for B and Si) when correlation is included, regardless of which correlation functional is employed in the calculations. Although there are minor changes in the results, the mre values are slightly worse than those obtained with the HF exchange for all of the functionals.

Regarding *A*, the Becke exchange stabilizes the anion with respect to HF, so that the *A* values obtained with the former are always greater than those using the HF exchange for the systems under consideration. This is particularly important in B, C, N, O, F, and P. The average effect on each correlation functional depends on the *A* values obtained using the HF exchange. Hence, although the good results obtained with the VWN functional are worsened throughout almost the whole set of atoms, the underestimated results obtained using the LYP correlation functional and the HF exchange are corrected when the Becke exchange is used. This explains the remarkable worsening (improvement) in the mre for VWN (LYP) with respect to HF exchange. The *A* values obtained with F1(5) improve when the Becke exchange is used, except for B, S, and Cl.

The $\bar{\alpha}$ values are slightly modified, on average, although there are important changes in individual atoms. The Becke exchange functional seems to favor in/out correlation, thus improving the $\bar{\alpha}$ values for the right-hand side of the rows. On the contrary, the Becke exchange leads to a poor angular correlation, as evidenced by the loss of accuracy on the left-hand side of the rows. Although the last effect is more pronounced in F1(5) and

LYP, worsening their average results, the first one dominates in VWN, which gives slightly better values, on average.

Conclusions

Self-consistent field calculations of the HFKS-type using TBDF and other correlation functionals, together with extended basis sets, are able to give good results, with chemical accuracy for I , and good agreement for dipole polarizabilities. The difficulties in describing nondynamical correlation effects in the anion are responsible of the lack of agreement between exact and calculated A . On the other hand, the calculations carried out in this work imply a much less demanding computational effort than other *ab initio* methods.

The virial theorem plays an important role in the deduction of our TBDF functionals, and in this sense the good virial ratios obtained with eq. (11) are quite satisfactory.

The exchange contribution employed (HF or Becke) has little influence on the average values of I , with A and $\bar{\alpha}$ being the properties that depend more on the type of exchange. The Becke exchange shifts the A to higher values, due to the stabilization of the anion, improving the LYP results, which are underestimated by Hartree–Fock exchange. In contrast, this shift worsens the A provided by HF-VWN calculations, whereas the results obtained for F1(5) are slightly altered, on average, by the exchange. It seems that the Becke exchange accounts for the in/out correlation effects on $\bar{\alpha}$, at the cost of worsening the description of the angular correlation, having little influence on the average results.

Although the primary purpose of the TBDFs was their use in combination with multideterminant reference wave functions,⁴⁵ the results reported in this work show that they can also provide good estimates when just one Slater determinant is used. The local TBDF F1(5) gives very good results, with the same quality as those obtained with the nonlocal LYP functional. This, and the fact that TBDFs are sensitive to the multideterminant character of the wave function, thus taking into account the nondynamical correlation,^{41–45} make it a valuable tool in applications to atomic and molecular properties. Molecular calculations using the procedure described in this work are given in part II of this series.

Appendix A: Correlation Potentials of TBDF

In this section we give the expressions for the first derivative of the correlation energy functionals of ref. 1 with respect to ρ_α^0 . The corresponding derivative with respect to ρ_β^0 can be obtained from that with respect to ρ_α^0 , simply by interchanging ρ_β^0 and ρ_α^0 . Within the prescriptions made in the Introduction, the two-body density can be approximated by:

$$\rho_2(\mathbf{R}, r) = \rho_2^0(\mathbf{R}) P(\mathbf{R}, r) \exp(-r^2/\gamma(\mathbf{R})) \cdot [1 + F(\mathbf{R}, r)] \quad (\text{A1})$$

where the correlation factor $F(\mathbf{R}, r)$ is given by:¹

$$F(\mathbf{R}, r) = \Lambda^2(\mathbf{R}, r) - 2\Lambda(\mathbf{R}, r) \quad (\text{A2})$$

with:

$$\Lambda(\mathbf{R}, r) = e^{-\beta^2(\mathbf{R})r^2} \cdot (1 - \Phi(\mathbf{R})f(r)) \quad (\text{A3})$$

and:

$$\beta(\mathbf{R}) = q\rho_0^{1/3}(\mathbf{R}) \quad (\text{A4})$$

with q being an adjustable parameter. If the reference charge- and two-body densities, $\rho^0(\mathbf{R})$ and $\rho_2^0(\mathbf{R})$, are those corresponding to one Slater determinant, the TBDFs of ref. 1 take the following form:

$$E_c = \int \varepsilon_c(\mathbf{R}) d\mathbf{R} \quad (\text{A5})$$

with:

$$\varepsilon_c(\mathbf{R}) = 2\pi\rho_\alpha(\mathbf{R})\rho_\beta(\mathbf{R})I(\mathbf{R}) \quad (\text{A6})$$

where $\rho_\alpha(\mathbf{R})$ and $\rho_\beta(\mathbf{R})$ are the spin-charge densities of the determinant, with

$$I(\mathbf{R}) = I_1(\mathbf{R})\Phi^2(\mathbf{R}) - 2I_2(\mathbf{R})\Phi(\mathbf{R}) - I_3(\mathbf{R}) \quad (\text{A7})$$

and:

$$\Phi(\mathbf{R}) = \frac{C_2(\mathbf{R}) + \sqrt{C_2^2(\mathbf{R}) + C_1(\mathbf{R})C_3(\mathbf{R})}}{C_1(\mathbf{R})} \quad (\text{A8})$$

The functional derivative of eq. (A5) with respect to ρ_α is given by:

$$\frac{\delta E_c}{\delta \rho_\alpha} = \frac{\partial \varepsilon_c}{\partial \rho_\alpha} = 2\pi\rho_\beta \left(I + \rho_\alpha \frac{\partial I}{\partial \rho_\alpha} \right) \quad (\text{A9})$$

$$\frac{\partial I}{\partial \rho_\alpha} = \left(\Phi^2 \frac{\partial I_1}{\partial \rho_\alpha} - 2\Phi \frac{\partial I_2}{\partial \rho_\alpha} - \frac{\partial I_3}{\partial \rho_\alpha} \right) + 2(I_1\Phi - I_2) \frac{\partial \Phi}{\partial \rho_\alpha} \quad (\text{A10})$$

$$\frac{\partial \Phi}{\partial \rho_\alpha} = -\frac{1}{2(C_1\Phi - C_2)} \times \left(\Phi^2 \frac{\partial C_1}{\partial \rho_\alpha} - 2\Phi \frac{\partial C_2}{\partial \rho_\alpha} - \frac{\partial C_3}{\partial \rho_\alpha} \right) \quad (\text{A11})$$

The explicit form of the functions I_i , $\partial I_i/\partial \rho_\alpha$, C_i , and $\partial C_i/\partial \rho_\alpha$ ($i = 1, 2, 3$) depends on the expression taken for $f(r)$, a function that modifies the original expression of the correlation factor $F(\mathbf{R}, r)$ used by Colle and Salvetti.^{3,4}

POLYNOMIAL $f(r)$

$$f(r) = 1 + \frac{1}{2}r + b_2r^2 + \dots + b_jr^j + \dots \quad (\text{A12})$$

This form of $f(r)$ leads to the F1-type of functionals, for which the expressions of the aforementioned functions take the form:

$$I_1 = \frac{1}{2} \sum_{ijl} a_i b_j b_l \cdot \Gamma((i+j+l+2)/2) \cdot \varepsilon^{-(i+j+l+2)/2} \quad (\text{A13})$$

$$I_2 = \frac{1}{2} \sum_{ij} a_i b_j \cdot \Gamma((i+j+2)/2) \cdot (\varepsilon^{-(i+j+2)/2} - \sigma^{-(i+j+2)/2}) \quad (\text{A14})$$

$$I_3 = \frac{1}{2} \sum_{i=0} a_i \cdot \Gamma((i+2)/2) \cdot (2\sigma^{-(i+2)/2} - \varepsilon^{-(i+2)/2}) \quad (\text{A15})$$

$$\frac{\partial I_1}{\partial \rho_\alpha} = \frac{1}{2} \sum_{ijl} b_j b_l \Gamma((i+j+l+2)/2) \varepsilon^{-(i+j+l+2)/2} \times \left[\frac{\partial a_i}{\partial \rho_\alpha} + \frac{(i+j+l+2)}{2} a_i \left(\frac{-1}{\varepsilon} \frac{\partial \varepsilon}{\partial \rho_\alpha} \right) \right] \quad (\text{A16})$$

$$\frac{\partial I_2}{\partial \rho_\alpha} = \frac{1}{2} \sum_{ij} b_j \Gamma((i+j+2)/2) \times \left[\frac{\partial a_i}{\partial \rho_\alpha} (\varepsilon^{-(i+j+2)/2} - \sigma^{-(i+j+2)/2}) - \frac{(i+j+2)}{2} a_i \times \left(\frac{\partial \varepsilon}{\partial \rho_\alpha} \varepsilon^{-(i+j+4)/2} - \frac{\partial \sigma}{\partial \rho_\alpha} \sigma^{-(i+j+4)/2} \right) \right] \quad (\text{A17})$$

$$\frac{\partial I_3}{\partial \rho_\alpha} = \frac{1}{2} \sum_i \Gamma((i+2)/2) \times \left[\frac{\partial a_i}{\partial \rho_\alpha} (2\sigma^{-(i+2)/2} - \varepsilon^{-(i+2)/2}) - \frac{(i+2)}{2} a_i \times \left(2 \frac{\partial \sigma}{\partial \rho_\alpha} \sigma^{-(i+4)/2} - \frac{\partial \varepsilon}{\partial \rho_\alpha} \varepsilon^{-(i+4)/2} \right) \right] \quad (\text{A18})$$

where Γ represents the Gamma function, while ε , and σ are given by:

$$\varepsilon(\mathbf{R}) = 2\beta^2(\mathbf{R}) + \gamma(\mathbf{R})^{-1} \quad (\text{A19a})$$

$$\sigma(\mathbf{R}) = \beta^2(\mathbf{R}) + \gamma(\mathbf{R})^{-1} \quad (\text{A19b})$$

C_1 , C_2 , C_3 , and the corresponding derivatives can be obtained from eqs. (A13)–(A18), respectively, simply replacing i by $i+1$. In eq. (A12), the b_i coefficients are adjustable parameters.

EXPONENTIAL $f(r)$

$$f(r) = \exp(r/2) \quad (\text{A20})$$

This expression for $f(r)$ leads to the F2-type functionals, with:

$$I_1 = e^{1/8\varepsilon} \sum_i a_i \cdot \Gamma(i+2) \cdot (2\varepsilon)^{-(i+2)/2} \cdot D_{-(i+2)}(-1/\sqrt{2\varepsilon}) \quad (\text{A21})$$

$$I_2 = \sum_i a_i \cdot \Gamma(i+2) \times \left[e^{1/32\varepsilon} \cdot (2\varepsilon)^{-(i+2)/2} \cdot D_{-(i+2)}(-1/2\sqrt{2\varepsilon}) - e^{1/32\sigma} \cdot (2\sigma)^{-(i+2)/2} \cdot D_{-(i+2)}(-1/2\sqrt{2\sigma}) \right] \quad (\text{A22})$$

while I_3 retains the form in eq. (A18). When obtaining the derivatives of the previous functions,

we use the following relations for the parabolic cylinder functions, $D_n(x)$:⁴⁶

$$D_0(x) = \exp(-x^2/4) \quad (\text{A23a})$$

$$D_{-1}(x) = (\pi/2)^{1/2} \exp(x^2/4) [1 - \operatorname{erf}(x/\sqrt{2})] \quad (\text{A23b})$$

$$D_{n+1}(x) - xD_n(x) + nD_{n-1}(x) = 0 \quad (\text{A23c})$$

where n is an integer, x a real number, and erf , the error function. Therefore,

$$\begin{aligned} \frac{\partial I_1}{\partial \rho_\alpha} = & e^{1/8\varepsilon} \sum_i \Gamma(i+2) \cdot (2\varepsilon)^{-(i+2)/2} \\ & \times \left[\frac{(i+2)(i+3)}{2} a_i D_{-(i+4)} \right. \\ & \times (-1/\sqrt{2\varepsilon}) \left(\frac{-1}{\varepsilon} \frac{\partial \varepsilon}{\partial \rho_\alpha} \right) \\ & \left. + \frac{\partial a_i}{\partial \rho_\alpha} D_{-(i+2)} (-1/\sqrt{2\varepsilon}) \right] \quad (\text{A24}) \end{aligned}$$

$$\begin{aligned} \frac{\partial I_2}{\partial \rho_\alpha} = & \sum_i \Gamma(i+2) \\ & \times \left\{ I_2^i \frac{\partial a_i}{\partial \rho_\alpha} - a_i (i+2)(i+3) \right. \\ & \times \left[e^{1/32\varepsilon} (2\varepsilon)^{-(i+4)/2} D_{-(i+4)} \right. \\ & \times (-1/2\sqrt{2\varepsilon}) \frac{\partial \varepsilon}{\partial \rho_\alpha} - e^{1/32\sigma} (2\sigma)^{-(i+4)/2} \\ & \left. \left. \times D_{-(i+4)} (-1/2\sqrt{2\sigma}) \frac{\partial \sigma}{\partial \rho_\alpha} \right] \right\} \quad (\text{A25}) \end{aligned}$$

where I_2^i is the expression between brackets of eq. (A22).

The corresponding expressions for C_1 , C_2 , and its derivatives can be obtained from eqs. (A21)–(A25) by replacing i with $i+1$. C_3 and its derivative are the same as those derived for the polynomial $f(r)$. ε and σ are given by eq. (A19).

SOME DERIVATIVES COMMON TO BOTH SETS OF FUNCTIONALS

In ref. 1, we developed the correcting polynomial of eq. (A1) up to as much as third order; that is, $P(\mathbf{R}, r) = 1 + a_1(\mathbf{R})r + a_2(\mathbf{R})r^2 + a_3(\mathbf{R})r^3$, with

a_1 , a_2 , and a_3 given by:

$$a_1(\mathbf{R}) = p_1/\gamma^{1/2}(\mathbf{R}) \quad (\text{A26})$$

$$a_2(\mathbf{R}) = p_2/\gamma(\mathbf{R}) \quad (\text{A27})$$

$$a_3(\mathbf{R}) = -\frac{\pi^{1/2}(1-k^{-3/2})}{4\gamma^{3/2}(\mathbf{R})} - \frac{a_1}{2\gamma(\mathbf{R})} - \frac{3\pi^{1/2}a_2}{8\gamma^{1/2}(\mathbf{R})} \quad (\text{A28})$$

This choice gives rise to the F1(6) and F2(5) functionals. If only two terms are selected, then:

$$a_1(\mathbf{R}) = p_1/\gamma^{1/2}(\mathbf{R}) \quad (\text{A29})$$

$$a_2(\mathbf{R}) = -\frac{2(1-k^{-3/2})}{3\gamma(\mathbf{R})} - \frac{4a_1}{3(\pi\gamma(\mathbf{R}))^{1/2}} \quad (\text{A30})$$

and we have the F1(5) functional. In the above expressions, $\gamma(\mathbf{R})$ is given by:

$$\gamma(\mathbf{R}) = k\gamma^0(\mathbf{R}) \quad (\text{A31})$$

$$\gamma^0(\mathbf{R}) = \frac{1}{\pi} \left(\frac{(N-1)\rho^0(\mathbf{R})}{2\rho_2^0(\mathbf{R})} \right)^{2/3} \quad (\text{A32})$$

where k and p_i are adjustable parameters.

Thus, the corresponding derivatives of a_i ($i = 1, 2$, or 3) are given by:

$$\frac{\partial a_i}{\partial \rho_\alpha} = \frac{i}{3} a_i \frac{\rho_\beta}{\rho \rho_\alpha} \quad (\text{A33})$$

Finally, the derivatives of ε and σ with respect to ρ_α , are as follows:

$$\frac{\partial \varepsilon}{\partial \rho_\alpha} = \frac{2}{3\rho} \left[\varepsilon + \frac{1}{\gamma} \left(\frac{\rho_\beta}{\rho_\alpha} - 1 \right) \right] \quad (\text{A34})$$

$$\frac{\partial \sigma}{\partial \rho_\alpha} = \frac{2}{3\rho} \left[\sigma + \frac{1}{\gamma} \left(\frac{\rho_\beta}{\rho_\alpha} - 1 \right) \right] \quad (\text{A35})$$

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